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著者	Suzuki K., Kataoka N., Inoue A., Makino A., Masumoto T.
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RAPID PUBLICATION

High Saturation Magnetization and Soft Magnetic Properties of bcc Fe–Zr–B Alloys with Ultrafine Grain Structure

By K. Suzuki*†, N. Kataoka*, A. Inoue*, A. Makino** and T. Masumoto*

A new soft magnetic material exhibiting high magnetizations (B_{800}) of 1.60 to 1.70 T under an applied field of 800 kA/m as well as high effective permeabilities (μ_e) of 13000 to 15000 at 1 kHz was produced in Fe–Zr–B alloys ranging from 5 to 7 at% Zr and 2 to 6%B. The material consists of a bcc phase produced by annealing the melt-spun Fe–Zr–B amorphous ribbons for 3.6 ks in the range of 873 to 923 K and the grain size is as small as 15 to 20 nm. The lattice parameter of the bcc phase is about 0.2870 nm which is larger than that of pure α-Fe. The crystallization-induced bcc phase is a metastable phase saturated with the solute elements and the annealing at temperatures above 973 K brings about a decomposition of the bcc phase to α-Fe and Fe_3Zr, leading to a drastic decrease of μ_e. The bcc Fe–Zr–B alloys possess B_{800} and μ_e much higher than those of Fe–Si–B amorphous alloys and hence are highly attractive as a new soft magnetic material.

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I. Introduction

It is generally known that soft magnetic amorphous alloys can be classified into two groups of Fe-based alloys with high saturation magnetization (B_s) and Co-based alloys with high effective permeability (μ_e). Consequently, in order to produce a soft magnetic material with high B_s, researches have been carried out mainly for Fe-rich alloys. When attention is paid to the Fe concentration which is a dominant factor in B_s, the Fe content leading to the formation of an amorphous phase by melt spinning is in the range of 88 to 91 at% in Fe–Zr[1] and Fe–Hf[2] systems, being considerably higher than that (70 to 80%) in an Fe-metalloid system. The addition of a small amount of B to Fe–Zr and Fe–Hf alloys has been reported to bring about an amorphous phase having good soft magnetic properties and an enhanced glass-forming capacity[3][4]. Although the B_s at room temperature for Fe-rich Fe–Zr and Fe–Hf amorphous alloys is considerably lower than that of Fe–Si–B amorphous alloys because of the Invar effects[5]-[7] leading to the decrease of Curie temperature and magnetic moment, it is very likely that a bcc solution in the Fe-rich Fe–Zr–B and Fe–Hf–B systems exhibits high B_s. Furthermore, when the bcc solution exhibits magnetostriction smaller than that (1.0×10^{-5} to 2.7×10^{-5})[3] for Fe–Zr–B and Fe–Hf–B amorphous alloys, the μ_e is also expected to have a rather high value.

It is known that an ultrafine grain structure consisting only of a bcc phase can be formed upon low-temperature annealing of Fe–Si–B amorphous alloys[8]. Subsequently, the precipitation of fine bcc grains in the Fe–Si–B amorphous matrix has been reported[9][10] to bring about the improvement of the soft magnetic properties as compared with the Fe–Si–B amorphous single phase. There is a report[11] that the soft magnetic properties are improved through the reduction of apparent crystal magnetic anisotropy in the crystalline magnetic thin films with ultrafine grain structure. It has recently been found[12][13] that the bcc phase alloys consisting of ultrafine grain structure, which was produced by crystallization of Fe–Si–B amorphous alloys containing 3%Nb and 1%Cu, exhibit good soft magnetic properties with B_s of about 1.3 T and μ_e of 100000 at 1 kHz. The simultaneous addition of Nb and Cu elements is essential to obtain the bcc single phase exhibiting the good soft magnetic properties upon short-time annealing and the reason for the achievement of the good soft magnetic properties has been attributed[12]-[15] to the bcc Fe(Si) solid solution with significantly reduced magnetic anisotropy resulting from the ultrafine equiaxed grain structure. A similar improvement of the soft magnetic properties has also been confirmed[16] for vapor-deposited Fe–Zr and Fe–Hf films consisting of an ultrafine bcc grain structure. More recently,

* Institute for Materials Research, Tohoku University, Sendai 980, Japan.
** Research and Development, Alps Electric Co., Ltd., Nagaoka 940, Japan.
† On leave from Alps Electric Co., Ltd., Nagaoka 940, Japan.

the present authors have systematically examined the crystallization-induced phases and the change in the magnetic properties caused by the precipitation of their crystalline phases in Fe–Zr–B and Fe–Hf–B ternary alloys in which the amorphous phase is formed at about 90%Fe higher than that of the Fe–Si–B system. As a result, we have succeeded in producing a new type of soft magnetic material exhibiting simultaneously B_s above 1.65 T and μ_e above 13000 at 1 kHz in Fe–Zr–B alloys with a bcc structure. This paper is intended to present the microstructure and magnetic properties of the bcc phase produced by crystallization of amorphous Fe–Zr–B alloys.

II. Experimental Procedure

Fe–Zr–B and Fe–Hf–B ternary ingots were produced by arc melting mixtures of pure Fe and Zr (or Hf) metals and pure B crystal in an argon atmosphere. The subscripts are assumed to be those of the unalloyed pure elements since the difference between nominal and chemically analyzed compositions was less than 0.8 mass% for Zr and 0.1 mass% for B. Rapidly solidified ribbons with a cross section of about 0.02×1 mm were produced in an argon atmosphere by a single-roller melt spinning method. The as-quenched samples were subjected to heating for 3.6 ks at various temperatures inside a vacuum-sealed quartz tube, followed by water quenching. As-quenched and annealed structures were examined by X-ray diffractometry using Cu Kα radiation, transmission electron microscopy (TEM) and differential thermal analysis (DTA). Magnetization under an applied field of 800 kA/m (B_{800}) and coercive force (H_c) under 800 A/m were measured at room temperature with a vibrating sample magnetometer and a B–H loop tracer, respectively. In addition, effective permeability at 1 kHz under 0.8 A/m was measured at room temperature with a vector impedance analyzer.

III. Results and Discussion

1. Changes in the microstructure and magnetic properties upon annealing

An amorphous phase in the Fe–Zr–B system by melt spinning was formed in a wide compositional range of 9 to 12%Zr and 13 to 25%B[3]. Crystallization behavior of an $Fe_{91}Zr_7B_2$ amorphous alloy was examined at a heating rate of 0.17 K/s by differential thermal analysis. The alloy crystallizes through two exothermic peaks which appear in the temperature ranges of 752 to 780 K and 997 to 1022 K. The first and second peaks were confirmed to result from the phase transition of amorphous to bcc phases and bcc to α-Fe+Fe_3Zr phases, respectively, by X-ray diffractometry and TEM. It is thus notable that the bcc single phase exists in the wide temperature range of 780 to 997 K. In order to confirm the high thermal stability of the metastable bcc phase obtained by crystallization of the Fe–Zr–B amorphous alloy and to establish an

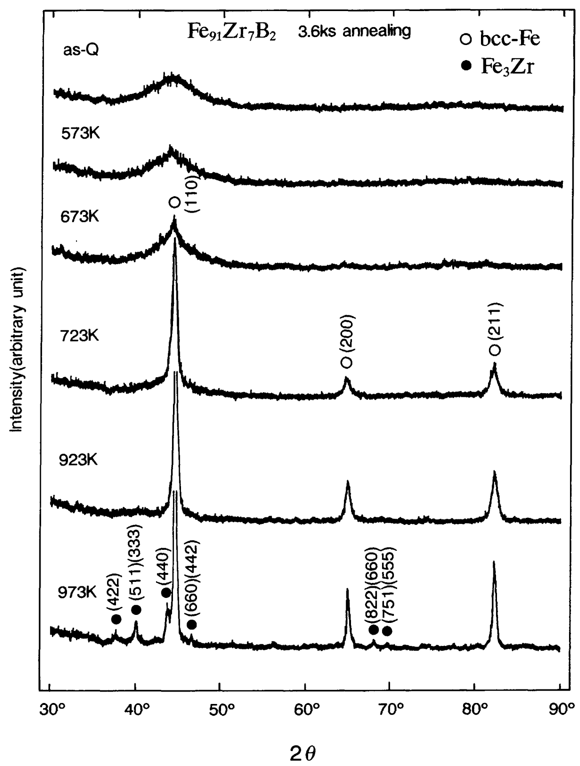

Fig. 1 Change in the X-ray diffraction patterns of an $Fe_{91}Zr_7B_2$ amorphous alloy with annealing temperature.

optimum condition to obtain the bcc phase by isothermal annealing, structural change upon annealing for 3.6 ks at various temperatures was examined by X-ray diffraction and TEM techniques.

Figure 1 shows the change in X-ray diffraction patterns of an $Fe_{91}Zr_7B_2$ amorphous alloy upon annealing at the temperatures ranging from 573 to 973 K. The amorphous phase remains almost unchanged at temperatures below 673 K and changes clearly to a mostly single bcc phase at 723 K. The bcc phase decomposes into a mixed structure of α-Fe and Fe_3Zr at 973 K. The lattice parameter of the bcc phase obtained by annealing for 3.6 ks at 873 K is 0.2870 nm which is considerably larger than that (0.2866 nm)[17] for pure α-Fe. The large lattice parameter indicates that the bcc phase dissolves the solute elements above an equilibrium soluble limit.

Figure 2(a) and (b) shows the magnetization under an applied field of 800 kA/m (B_{800}) and the effective permeability at 1 kHz (μ_e) as a function of annealing temperature (T_a) for a melt-spun $Fe_{91}Zr_7B_2$ alloy. As shown in Fig. 2(a), the B_{800} remains constant ($\simeq 0.2$ T) in the temperature range below 673 K, increases rapidly to about 1.25 T in the narrow range of 673 to 723 K and then gradually to 1.70 T with an increase of T_a to 923 K. The temperature range leading to the drastic increase of B_{800} agrees well with that in which the amorphous phase changes to the bcc phase and hence the increase in B_{800} is concluded to originate from the phase transition from the amorphous phase with the Invar effects[5]-[7] to the bcc supersaturated solution with ordinary ferromagnetism. As shown in Fig. 2(b), the μ_e for the $Fe_{91}Zr_7B_2$ amor-

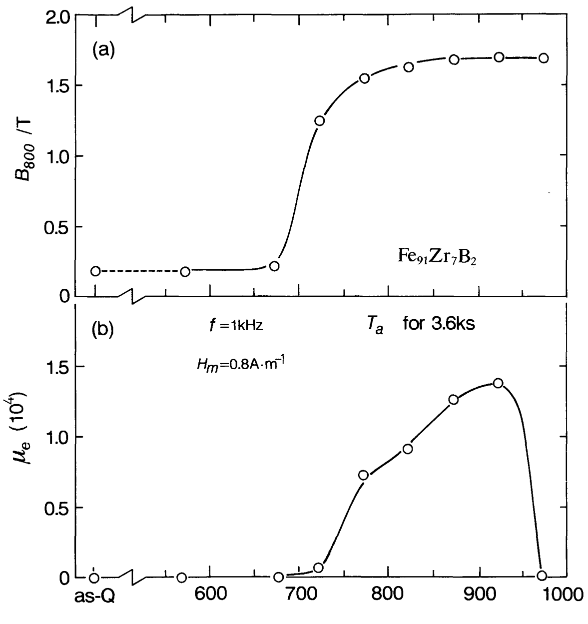

Fig. 2 (a) magnetization (B_{800}) under an applied field of 800 kA/m and (b) effective permeability μ_e at 1 kHz and 0.8 A/m as a function of annealing temperature for an $Fe_{91}Zr_7B_2$ amorphous alloy.

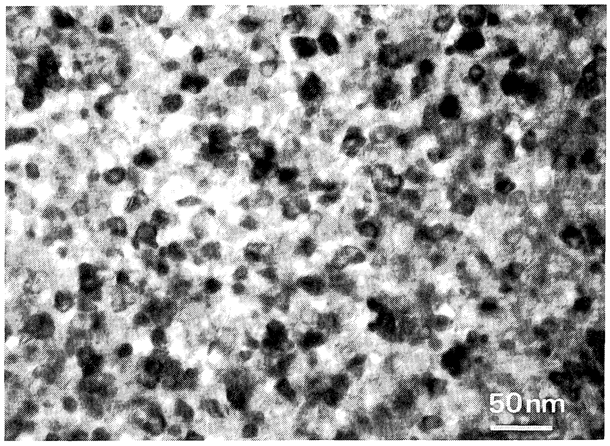

Fig. 3 Bright-field electron micrograph of an $Fe_{91}Zr_7B_2$ amorphous alloy annealed for 3.6 ks at 923 K.

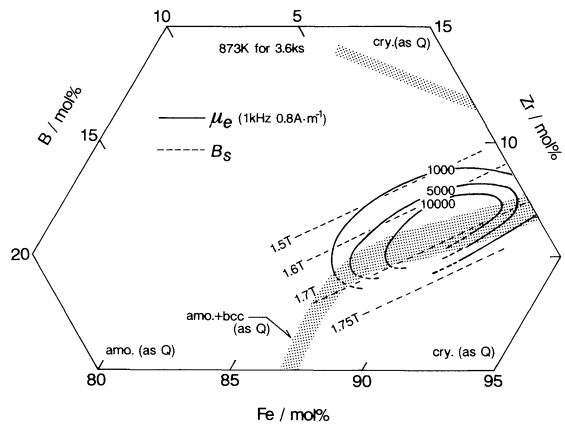

Fig. 4 Compositional dependences of B_{800} and μ_e for melt-spun Fe–Zr–B alloys annealed for 3.6 ks at 873 K.

phous alloy begins to increase upon the phase transition of amorphous to amorphous plus bcc phases, shows a maximum value of 14000 at 923 K for the mostly single bcc phase and then decreases drastically by the decomposition into α-Fe and Fe_3Zr. It should be noted that the highest μ_e value (14000) attained for the bcc solution exceeds largely the μ_e value ($\simeq 6000$)[18] for Fe–Si–B amorphous alloys with a rather high B_s of 1.4 T.

The half width of the (110) diffraction peak for the bcc solution obtained by annealing for 3.6 ks at 923 K is 0.54 degree for $Fe_{91}Zr_7B_2$ and the grain size of the bcc phase is evaluated to be as small as 18 nm from the half width value by using Scherrer's equation[19], indicating that the dissolution of Zr and B elements results in a refinement of grain size of the bcc phase. In order to confirm the ultrafine grain structure, TEM observation was made for the bcc $Fe_{91}Zr_7B_2$ alloy annealed for 3.6 ks at 923 K. As exemplified in Fig. 3, the bcc phase is very homogeneous and consists of equiaxed grains with a size as small as about 17 nm, being consistent with the structure derived from the X-ray diffractometry. The reason why the bcc Fe–Zr–B alloy with ultrafine grain structure exhibits good soft magnetic properties is presumably due to a decrease of apparent anisotropy through the suppression of the magnetocrystalline anisotropy caused by the refinement of grain size. Furthermore, the reason for the rapid decrease in μ_e at 973 K is due to the formation of the mixed structure consisting of α-Fe and Fe_3Zr as well as to the increase of grain size of α-Fe to about 50 nm.

2. Compositional effect on the magnetic properties

Figure 4 shows the compositional dependences of B_{800} and μ_e for $Fe_{100-x-y}Zr_xB_y$ amorphous alloys subjected to annealing for 3.6 ks at 873 K leading to the formation of the bcc phase, along with the data of rapidly solidified phases. The amorphous phase is formed in a wide composition range of 8 to 11%Zr and 13 to 25%B and the further decrease in solute content from the minimum content ($\simeq$8at%) for formation of the amorphous phase brings about the formation of bcc supersaturated solution through a mixed structure of amorphous and bcc phases. The glass-formation range is in agreement with that for Fe–Zr–B alloys reported previously by Ohnuma *et al.*[3] In addition, the regions marked with dotted lines denote a coexistent region of amorphous and crystalline phases. As is evident from the contour lines of μ_e value, high μ_e values above 10000 are obtained in the compositional ranges in which the rapidly solidified phase consists of either an amorphous single phase or coexistent amorphous and bcc phases, indicating that the formation of an amorphous single phase is not always necessary for the achievement of the good soft magnetic properties. The μ_e value is strongly dependent on Zr concentration and the high μ_e values above 10000 are obtained in a narrow Zr range of 5 to 7%. The deviation of Zr content from the composition range brings about a rapid

Table 1 Magnetic properties, structure and sample thickness (t) of Fe–Zr–B and Fe–Hf–B alloys and other soft magnetic alloys.

Alloy	Structure	$t(\mu m)$	$B_s(T)$	μ_e at 1 kHz	$H_c(A\cdot m^{-1})$
$Fe_{91}Zr_7B_2$	bcc	18	1.70	14000	7.2
$Fe_{89}Zr_7B_4$	bcc	19	1.65	15000	7.4
$Fe_{89}Zr_5B_6$	bcc	16	1.70	13000	8.3
$Fe_{91}Hf_7B_2$	bcc	18	1.60	18000	4.1
Fe–6.5 mass% Si	Ordered bcc	300	1.80	2400	9.6
Fe–Si–B*	Amorphous	20	1.41	6000**	6.9
Co–Fe–Si–B*	Amorphous	18	0.53	80000**	0.32
$Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$*	bcc	18	1.24	100000**	0.53
$Fe_{81}Si_2B_{13}Nb_3Cu_1$*	bcc	18	1.55	9000**	12.8

*Ref. (18), ** $H_m=0.4\ A\cdot m^{-1}$

decrease in μ_e. On the other hand, the B_{800} value increases monotonically from 1.50 to 1.75 T with increasing Fe content from 85 to 93%.

Table 1 summarizes the structure, sample thickness and magnetic properties of Fe–Zr–B and Fe–Hf–B alloys, along with the data[18] of other typical soft magnetic materials including bcc Fe–Si–B–Nb–Cu alloys with ultrafine grain structure. The B_s values of the bcc Fe–Zr–B alloys are considerably higher than those of the bcc Fe–Si–B–Nb–Cu alloys and approaches that of Fe–6.5%Si. Furthermore, the μ_e values exceed largely those of Fe–6.5%Si and Fe-based amorphous alloys. Similar B_s and μ_e values are also obtained for an $Fe_{91}Hf_7B_2$ alloy with the same ultrafine bcc structure, as shown in Table 1. These data allow us to conclude that the bcc Fe–Zr–B and Fe–Hf–B alloys are a new type of soft magnetic material which does not belong to the groups of Fe- and Co-based amorphous alloys as well as bcc Fe–Si–B–Nb–Cu and Fe–Si alloys.

In conclusion, a new soft magnetic material exhibiting a high B_{800} of 1.70 T as well as a high μ_e of 14000 was produced for the bcc phase obtained by crystallization of a melt-spun $Fe_{91}Zr_7B_2$ amorphous alloy. The μ_e value is expected to increase further through the improvement of smoothness of the ribbon surface by adjusting the melt-spun condition. Further enhanced soft magnetic properties exhibiting higher B_s as well as higher μ_e have also been confirmed[20] to be obtained for the crystallization-induced bcc alloys in a number of alloy systems such as Fe–Zr–B–Cu, Fe–Hf–B–Cu, Fe–Zr–B–Cu–TM (TM=Nb, Ta or Mo), Fe–Hf–B–Cu–TM, Fe–Zr–B–Au and Fe–Hf–B–Au etc. An optimum alloy composition and the mechanism for the appearance of the good soft magnetic properties are under investigation.

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